

Project 45133

High-Pressure X-Ray Diffraction Characterization of Mt Elbert Cores Letter Report June 2009

H. T. Schaef and B. P. McGrail

Pacific Northwest National Laboratory, Richland, Washington

Introduction

In this letter report, core sediments from the Mt Elbert Stratigraphic Test Well #1 (Mt Elbert) located at Milne Point, Alaska were characterized *in situ* by high-pressure x-ray diffraction (HXRDX). These samples represent part of the 500 ft (152.4 m) of continuous core collected from the D and C sands in the Mikkelson Tongue of the Canning Formation (BOSWELL et al., 2008). Research teams began collecting core in February 2007 as part of a collaborative project aimed to assess the feasibility of gas hydrates as a future energy source. The well was drilled to a depth of 3,002 ft (915m), with 1,670 ft (509 m) of permafrost and several thick sand formations in an area of Prudhoe Bay estimated to contain between 35 and 42 trillion ft³ (1.0 and 1.2 trillion m³) of gas (RUTQVIST et al., 2009).

Two sandstone cores containing gas hydrate collected from Mt Elbert were transported in LN₂ dry dewars to PNNL for laboratory testing. These cores, currently maintained under LN₂, were sub-sampled and characterized for gas hydrate content along with other physical properties. The objective of this study was to utilize *in situ* HXRDX techniques developed at PNNL to examine natural gas hydrate rich sandstones under reservoir conditions (temperature and pressure). Observing and measuring gas hydrate dissociation in natural sediments by modifying *in situ* reservoir conditions are used to obtain information supportive of production concept studies and reservoir modeling.

Mt Elbert Core Sample Description

Two core samples collected from Mt Elbert were used in this study. A summary of the drilling operations and sample collection protocols is provided by Boswell et. al.(2008). Additional information on the well including well log data and physical measurements on select core samples can be found in Winters et. al., (2008), Lee and Waite (2008), Rutqvist et al., (2009) and Anderson et. al., (2008). Core sample designated as “HYD 8” [8_4_31_36], was preserved in LN₂ on site, and represents core 8, section 4 interval 31 to 36 inches. The actual core depth corresponds to 2,168.5 to 2,168.92 ft (660.96 to 661.07 m) with a log depth of 2,165.5 to 2,165.92 ft (660.04 to 660.17 m). The second core, “HYD 21” [7_4_14_22], was placed into a pressure vessel and pressurized with CH₄ on site and was not preserved in LN₂ until later. The corresponding core depth is 2,144.13 to 2,144.92 feet (653.53 to 653.77 m) with a log depth



Figure 1. Core “HYD 21” as received (preserved in LN₂).

of 2,141.13 to 2,141.92 ft (652.67 to 652.86 m). Figure 1 shows core HYD 21, which measured ~7 inches and was covered in brown drilling mud. HYD 8 appeared similar to HYD21 and also contained the brown coating. While working with these cores, staff noted a strong odor indicative of some volatile organic compound emitted from the cores when removed from LN₂.

Experimental Methods

Characterization of these hydrate rich core samples for this study included bulk powdered x-ray diffraction (XRD), clay mineralogy, bulk hydrate dissociation, and *in situ* HXRD. Small pieces of core were broken from the larger cores while being held at LN₂ temperature. Concentrating on the center section of each core, pieces were selected for bulk hydrate dissociation and HXRD experiments. Core pieces were placed into pre-chilled Parr pressure vessels (125 ml) and pressurized with deuterated methane (CD₄). Both reactors were placed into a Neslab RTE 7 at an initial temperature of -5°C. Temperature was increased in steps over a period of time up to 29°C. The remaining sections of each core were left intact and are being stored in LN₂.

Deuterated methane (Scott's Specialty Gases) was used in select experiments to track dissociation of natural methane hydrate. For these experiments, discrete gas samples were collected from the pressure cells at predetermined intervals, usually corresponding to temperature, and analyzed by a SRS RGA 200 (Stanford Research System) residual gas analyzer (RGA). HXRD experiments were done in Be-pressure cells and gas samples were collected directly from the cell by a Tescom Industrial Controls (Elk River, MN) valve (model CC-A16A21APB). After adjusting the valve to read a constant pressure of 10⁻⁴ Torr, data was collected every second for ten minutes for three atomic mass units: 15 (CH₃), 16 (CH₄), and 20 (CD₄). Data collected for each channel was corrected for isotopic abundance using the appropriate factor (CH₃-0.39568; CH₄-0.44964; and CD₄-0.44964). By averaging the corrected data from channel 20 and 15, a final partial pressure ratio of CH₄ to CD₄ was determined. Channel 16 was not used in the calculation because of the possibility of trace amounts of oxygen in the system. More detailed description on this procedure is found in McGrail et al., (2007).

Following bulk dissociation experiments, both vessels were depressurized to remove the core samples, which were then oven dried to determine moisture content. Sub-samples were removed for particle density measurements, bulk powder XRD, and clay separation. Density measurements were obtained on ~1 g samples (dried) and bulk XRD was conducted on 1 g samples (dried and crushed). Clay samples were prepared by separating the clay fraction (<2 μm) from the bulk sample using settling techniques. After a sufficient amount of clay was obtained from each sample, clay mounts were prepared following the procedure outlined by Moore and Reynolds (1989). Clay fractions were initially saturated with Mg⁺² cations prior to characterization by XRD. To distinguish the 12-15 Å swelling clays (smectites) from 14 Å non swelling clays (chlorites), ethylene glycol was added to the samples before analysis. X-ray diffraction patterns were obtained at 45kV and 40mA using a Scintag automated powder diffractometer (Model 3520) with nickel-filtered copper radiation, Cu K_{α1} radiation = 1.54 Å. The bulk powder samples were analyzed over a 2θ range of 2° to 65° with a step size of 0.04° and a two-second count time at each step. Clay mounts were analyzed from 2° to 45° 2θ. Scans were collected electronically and processed using the JADE[®] XRD pattern-processing software. Identification of the mineral phases in the patterns was based on a comparison of the XRD patterns with the mineral powder diffraction files (PDF[™]) published by the Joint Committee on Powder Diffraction Standards (JCPDS) International Center for Diffraction Data (ICDD)

(Newtown Square, Pennsylvania). Identification of clays minerals on the oriented clay mounts was based on the methodology presented by Moore and Reynolds (1989).

Samples for HXRD were small, typically measuring 3 mm by 4 mm and were taken from the center of both cores and kept in LN₂ until analyzed. The analyses were conducted on a Bruker-AXS Discover 8 x-ray diffraction (XRD) unit equipped with a custom built temperature stage (-110° to 225°C), rotating Co anode (18,000 watts), and a real time 2-dimensional area detector. The instrument, designed to analyze gas hydrate samples under reservoir conditions, uses x-ray transparent high-pressure beryllium cells that have been describe in previous letter reports. Initially the pressure cell is chilled in an ice bath prior to placing a small piece of hydrated sediment inside the sample cup. Dry liquid nitrogen vapor is constantly allowed to flow over the sample cup to maintain cryo temperatures. The sample cup is placed onto the beryllium cell before pressurization with CD₄. The HXRD experiments typically lasted several days with scans being collected every hour or half hour before increasing the temperature 1°C. Patterns were processed using JADE[®] XRD pattern-processing software as described earlier.

Sample Characterization

Core sediments were collected from gas hydrate rich section of Mt Elbert that consists of very fine grained, well sorted, quartz-rich sandstones (BOSWELL et al., 2008). For sample preservation purposes, sub-samples used in bulk hydrate dissociation experiments were utilized for physical property measurements.

Moisture content ranged between 18.6% and 20.0% and was similar for both samples (Table 1). Particle density measurements, 2.69-2.70 g/cm³, were almost identical to the value reported by Rutqvist et al., (2009). Porosity, values associated with gas hydrate bearing sandstone from Mt Elbert range between 25% and 45% (LEE and WAITE, 2008). Winters (2008) reported an average porosity value for the gas hydrate bearing zones of 42%. Using a known volume, dried sediment from HYD 21 was packed into cylinder. A calculated porosity of 47% was obtained. Although not as accurate as other methods, the results confirm the previously reported very high porosity of these unconsolidated sands.

Initial gas hydrate saturation (S_h^o) in these cores are estimated by the following expression:

Table 1. Physical characteristics measured from MT Elbert cores.

Analysis	Units	HYD 8	HYD 21
Moisture Content	%	18.6	20.0
Particle Density	g/cm ³	2.69	2.70
Clay Content	%	2	3
Hydrate Saturation	%	24	26

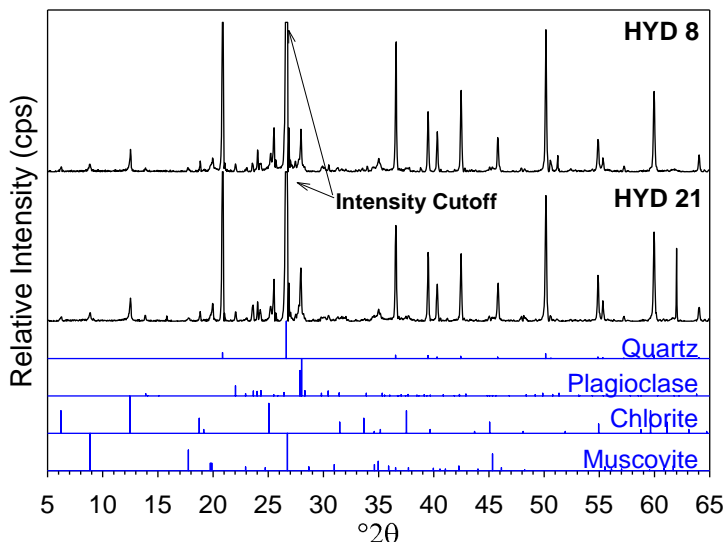


Figure 2. Bulk powder XRD results of HYD 8 Core showing the sediment is mostly quartz with lesser amounts of chlorite (clinochlore), muscovite, and plagioclase feldspar (albite) (based on Cu K_{α1} radiation, $\lambda=1.54 \text{ \AA}$).

$$S_h^o = S_w^o \times \frac{\rho_w^o}{\rho_h^o} = 0.2 \times \frac{1.01}{0.79} = 0.26$$

where S_w^o is initial water saturation, ρ_w^o is the initial density of the pore fluid phase, and ρ_h^o is the density of the S-I empty gas hydrate crystal lattice. This is a modified approach taken by McGrail et al., (2007), and provides an estimate for the maximum amount of gas hydrate in the samples by converting all available pore water into hydrate. Hydrate saturation determined for these cores is significantly less than reported from well log analysis (BOSWELL et al., 2008; LEE and WAITE, 2008). No laboratory measurements of gas hydrate saturations in sediment from Mt Elbert could be identified in published literature.

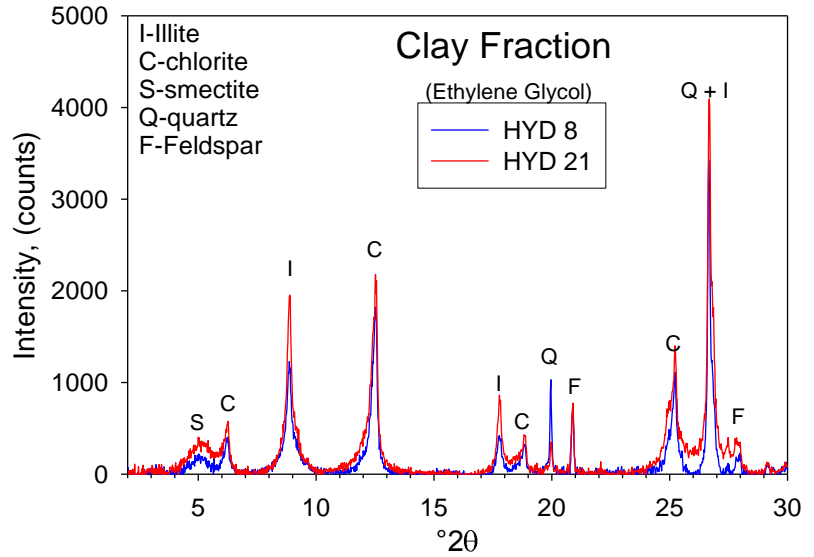


Figure 3. X-ray diffraction tracings from oriented clay mounts of clay fractions (Mg-saturated, ethylene glycol solvated) representing HYD 8 (black) and HYD 21 (blue) showing chlorite and muscovite as the dominate phases (based on Cu $K_{\alpha 1}$ radiation, $\lambda=1.54 \text{ \AA}$).

Bulk powder XRD confirmed these unconsolidated sands are similar and show the sediment is mostly quartz, with lesser amounts of chlorite, mica, and feldspar. The XRD tracing collected from HYD 8 is shown in Figure 2 along with PDF patterns of quartz [46-1045], albite [41-1480], muscovite [07-0042], and clinocllore [16-0362]. Quartz was identified by the primary reflection positioned at 3.34 \AA (Figure 2). The weak reflection at 3.17 \AA is from feldspar, most likely plagioclase (albite). Clays detected by bulk powder XRD were chlorite (clinocllore) and mica, which have primary first order reflections positioned at 14 \AA and 10 \AA , respectively (Figure 2). No reflections remained unassigned in these patterns.

X-ray diffraction was conducted on specially mounted clay fractions from both core samples. Intense reflections representing muscovite [07-0042] and chlorite [16-0362] indicate a binary clay system (Figure 3). The weak reflection at 18 \AA comes from a small amount of smectite. Based on the absence of a reflection positioned at 3.58 \AA , kaolinite was not detectable by XRD (Figure 3). Non clay minerals present in the clay fraction were minor amounts of quartz and feldspar (Figure 3).

Bulk Hydrate Dissociation Results

A limited amount of experimental work was conducted measuring bulk gas hydrate in relatively large core sediment samples (~60g). Core sub-samples were placed into reactors and quickly pressurized with CD₄ to 1,200-1,350 psi (8.27-9.31 MPa), and positioned into a chiller (-5°C). Discrete gas samples were collected at 1°C intervals every 24 hours (minimum) up to 29°C. Figure 4 shows results of the gas analysis as a function of temperature.

Between -5° to ~12°C, the measured CH₄/CD₄ ratio is constant and represents a base line of ~0.002. After reaching 12°C, the CH₄/CD₄ ratio for both samples starts to increase, representing the release of CH₄ into the reactor. This trend continues as the temperature increases, well beyond the stability field of methane gas hydrate (~12° to 15°C) under these pressures (SUN and DUAN, 2007). This behavior is highly unusual and atypical of similar experiments performed on other gas hydrate bearing sediment samples. Typically, the CH₄/CD₄ ratio increase corresponds to natural hydrate dissociation, which reaches a plateau near the bulk gas hydrate equilibrium temperature after all the gas hydrate has dissociated. Instead for the Mt Elbert samples, CH₄ concentrations continue to increase well past a temperature where any gas hydrate could physically remain in the system. Slow release of methane gas from the core interior due in part to disconnected porosity or reduced permeability could be one explanation. However, these cores were collected from unconsolidated porous sands with a reported average porosity of ~40% (WINTERS, 2008), where permeability (if the reported porosity values are correct) should be quite large.. Reactor temperatures were held at 29°C for 7 days to verify the ending CH₄/CD₄ ratios. Over the 7 day duration at 29°C, the average CH₄/CD₄ ratios were 0.069±0.007 (ME#21) and 0.033±0.004 (ME#8). Verification of the RGA measurements was done by measuring the starting gas ratio (Figure 4, solid red triangle) which was identical to the starting baseline. Pressure changes throughout the 42 day testing period are shown in Figure 4 (dashed lines) for each reactor. The increase in pressure observed throughout the duration of the experiment is due to the increase in temperature and represents ~20% increase. Our current hypothesis is that methane might be produced in the samples from methanogens consuming the organic compound that was apparently introduced in the drilling fluids used to extract the cores.

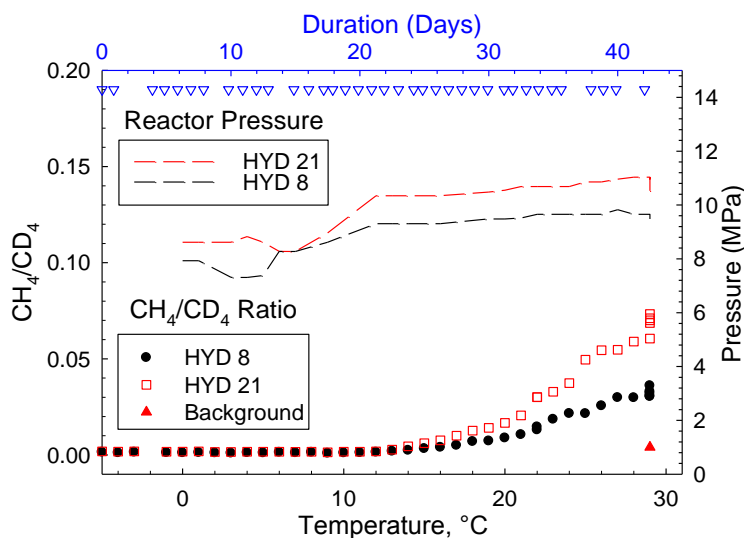


Figure 4 CH₄/CD₄ ratio determined by RGA from reactors containing HYD 8 and HYD 21 as a function of temperature (°C).

High Pressure X-Ray Diffraction Results

Characterization by HXRD was conducted on cores HYD 8 and HYD 21 to 1) verify the presence of natural gas hydrate, and 2) to measure the decomposition of methane gas hydrate as a function of temperature. Examination of a series of HXRD tracings collected at different temperatures (-5°, 1°, 7°, and 8°C) and corresponding pressures (6.09, 4.98, 4.77, and 4.76 MPa) from core HYD 8 show the presences of sI hydrate (Figure 5). For comparison purposes, reference patterns are provided for sI, and sII compounds along with water ice.

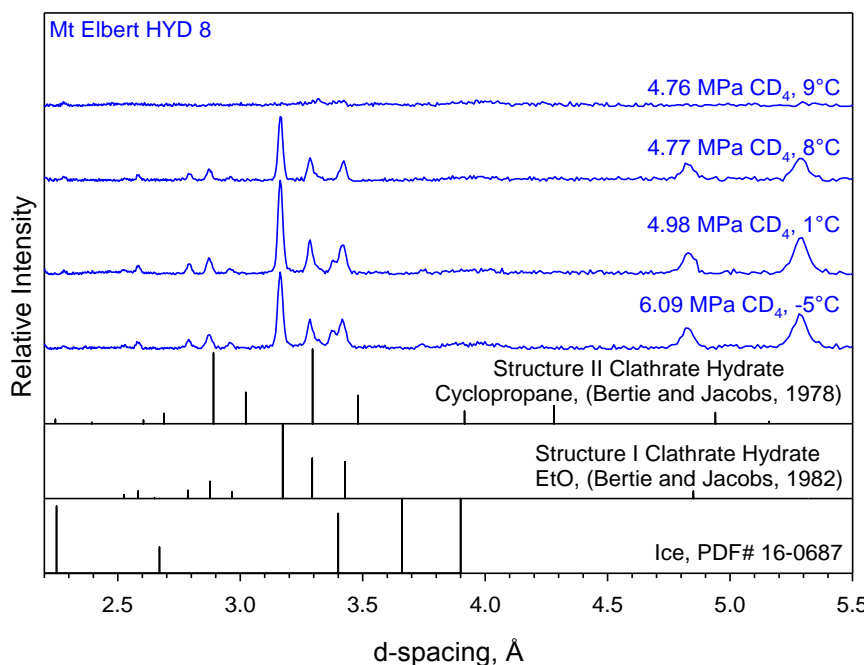


Figure 5. HXRD of Mt. Elbert HYD 8 collected from -5° to 9°C under an initial CD₄ gas pressure of 6.09 MPa (based on Co K_{α1} radiation, $\lambda=1.7889$ Å).

Core HYD 8, had the first pattern collected at -5°C; no evidence of water ice (PDF# 16-0687) was detected. Patterns collected at -5°, 1° and 8°C contain reflections assigned to sI hydrate. No other reflections were identified in these tracings. After increasing the temperature above 8°C, all reflections disappear indicating no detectable methane gas hydrate. For this experiment, the x-ray beam was focused on a pore space containing gas hydrate and not allowed to move vertical over the sample surface. Although the sample consisted of quartz, feldspar, and clays, these crystalline substances were not detected by XRD using this fine focused analytical technique. Following completion of the experiment, the x-ray beam was moved over the entire 4mm distance of the sample and reflections corresponding to quartz were observed.

Positive verification of gas hydrate in the sample is demonstrated by reflections corresponding to sI clathrate hydrate (Bertie and Jacobs, 1982) as seen from the 3D series of XRD patterns shown in Figure 7. The three most intense reflections for sI methane hydrate are positioned at 30.26°, 31.52°, and 32.79° 2 θ (based on Co K_{α1} radiation, $\lambda=1.7889$ Å), with relative peak intensities closely matching those calculated for sI hydrate by Bertie and Jacobs (1982). Minor reflections assigned to sI hydrate (19.45°, 21.30°, 35.11°, 36.16°, 37.31°, 40.45°, and 52.14° 2 θ) are also observed on the diffraction pattern at the lower temperatures (Figure 7). Increasing the temperature (1°C per 30 minutes) up to 8°C resulted in a slight decrease in sI peak intensities, indicating partial dissociation of sI gas hydrate. Reflections corresponding to sI methane hydrate completely disappeared at 9°C, indicating complete dissociation. Ideally the experiment would be conducted at a near constant pressure, however, a small leak developed in the reactor causing the pressure to drop 22%.

Experiments conducted with HYD 21 were performed slightly different. The micro-focused x-ray beam was moved vertically top to bottom over the sand, which measured slightly less than 4 mm in length. Reflections representing quartz and feldspar were initially detected along with sI gas hydrate within the temperature interval 1° to 8°C. This can be seen in Figure 6 by the intense reflections positioned at 31.46° and 32.99°2 θ (based on Co K $_{\alpha 1}$ radiation, $\lambda=1.7889$ Å). Above 8°C, gas hydrate was not detected, which is indicated by the increase in intensity for the primary quartz reflection (31.46°2 θ) and the near disappearance of the sI clathrate hydrate reflections at 32.99°2 θ . To track the CH $_4$ /CD $_4$ ratio, discrete gas samples were collected at each temperature. Over the temperature interval -2° to 15°C, the average CH $_4$ /CD $_4$ ratio was 0.00398 ± 0.00035 indicating no measurable release of naturally occurring CH $_4$ from gas hydrate.

Discussion

Literature reviews show sI gas hydrate as being detected by conventional XRD (ambient pressure) in natural sediments from hydrate ridge (BOHRMANN et al., 2007), lake bottom sediments (TAKEYA et al., 2005), ocean sediments (MATSUMOTO et al., 2000), and in synthetic samples (CIRONE et al., 2003; SUSILO et al., 2007; UCHIDA et al., 2007). *In situ* HXRD has been used to verify the presence of sI gas hydrate in synthetic and natural sediments using high energy x-rays typically available through specialized facilities (HENNING et al., 2000; HALPERN et al., 2001; HOSHIKAWA et al., 2006; THOMPSON et al., 2006; BOURRY et al., 2007). However, no previous instance could be identified where conventional XRD techniques were used in conjunction with x-ray transparent high pressure cells to characterize natural occurring gas hydrate rich sediments under pressure.

Core samples collected from gas-hydrate rich zones were unconsolidated well-sorted quartz sands with minor amounts of feldspar and clays (mica, chlorite, and smectite). Moisture contents were low (18-20%), which translated into 20-23% gas hydrate saturations, significantly lower

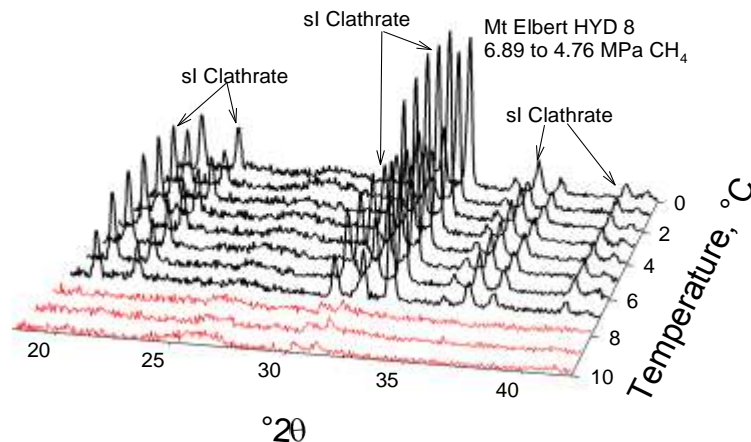


Figure 7. *In situ* HXRD of HYD 8 collected from -5° to 10°C over a CD $_4$ gas pressure interval of 6.89 to 4.76 MPa (based on Co K $_{\alpha 1}$ radiation, $\lambda=1.7889$ Å).

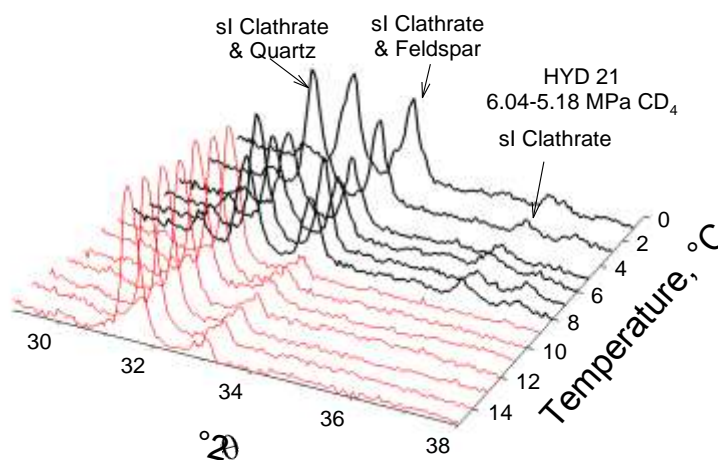


Figure 6. *In situ* HXRD of HYD 21 collected from 1° to 15°C over a CD $_4$ gas pressure interval of 6.04 to 5.18 MPa (based on Co K $_{\alpha 1}$ radiation, $\lambda=1.7889$ Å).

than 60-80% estimations obtained from well logs collected over the same depth intervals (BOSWELL et al., 2008). Hydrate bearing sediment collected for laboratory examination are often lacking in natural gas hydrate due to long core retrieval times, lengthy storage times in LN₂, or by simply overestimation. Bulk dissociation experiments are one method used to determine if naturally occurring gas hydrate remains in the sediment. Core HYD 8 was initially used in bulk dissociation tests during the later part of 2007, primarily to confirm the absence or presence of gas hydrate. A limited amount of sample (8.3 g) removed from the center of HYD 8 was used in a dissociation experiment with a starting CD₄ pressure of 6.49 MPa and temperature range of 0° to 20°C. The measured CH₄/CD₄ ratio was constant (0.001 to 0.002) for the temperature interval (0° to 15°C) during a 24 hour period. The final temperature, 20°C, was held for 4 days before a gas sample was collected, which contained a CH₄/CD₄ ratio of 0.023, over a 10 fold increase from earlier readings.

Bulk dissociation experiments conducted on larger amounts of core (~60 g) produced unexpected results. Between the temperature interval -5° to 12°C, the CH₄/CD₄ ratio remained nearly constant at ~0.003. A continuous increase in the CH₄/CD₄ ratio was observed for both samples starting at ~12°C until the final temperature of 29°C. Even while the temperature was held steady for 7 days, the ratio increased for both samples ~12%, indicating natural methane (CH₄) was being generated inside the vessels. As mentioned earlier, this is unusual compared to results reported by McGrail et. al., (2007) and Schaef et. al., (2008) where the dissociation of naturally occurring gas hydrate was observed continuously up to the bulk hydrate stability temperature, after which the CH₄/CD₄ ratio plateaued. Because no detectable gas hydrate dissociation occurred over the -5° to 12°C interval and the shorter duration HXRD experiments also showed no statistically significant change in the CH₄/CD₄ ratio, we conclude it unlikely these unconsolidated sandstones contained naturally occurring gas hydrate as shipped to PNNL from the drill site. However, this does not explain the repeated observations of CH₄/CD₄ ratio increase at temperatures above the hydrate stability point.

Using data from Figure 4, rates of methanogenesis can be estimated and compared to literature values (CRAGG et al., 1996; WELLSBURY et al., 1997; COLWELL et al., 2008). With a ~136.2 cm³ reactor, ~26 cm³ of sample (HYD 8), 0.82 CH₄ compressibility factor, the amount of CD₄ in the vessel (29°C and 9.65 MPa) was calculated at 0.516 moles. Based on RGA sample data between 910 and 933 hours, a CH₄/CD₄ ratio difference of 0.0025 translates into 0.00129 moles of CH₄. For comparison purposes, the cell population was taken at 1000 cells per g of sediment. The dry weight of HYD8 was 59.46 g. An estimated rate of methane production associated with HYD 8 is ~0.0217 nmol/g sediment/ day. Although these values are significantly higher than reported by Colwell et al (2008) on sediments at Hydrate Ridge (4.25 fmol/g sediment/day), they are similar to rates reported by Cragg et al.(1996), from hydrate samples collected at the Cascadia Margin (10⁻³ to 10⁻² nmol/g sediment/day). Residual mineral oil based drilling fluid introduced in the sample may well act as a nutrient source stimulating more rapid microbial metabolism than would occur naturally in these sediments. Additional characterization work is planned to verify our speculation on biogenic methane production in these samples.

The *in situ* HXRD application applied to these unconsolidated sandstones used x-ray transparent pressure cells to maintain pressure and temperature similar to known reservoir conditions (RUTQVIST et al., 2009). Attempts were made to select samples from the center of each core to allow for better odds at obtaining gas hydrate rich areas. Both samples appeared to

contain sI gas hydrate based on the HXRD results (Figure 7 and Figure 6). Reflections associated with water ice were not observed in either sample, even when examined below 0°C. However, residual gas samples collected from HYD 21 did not indicate a change in the CH₄/CD₄ ratio. Although the HXRD results verify the presence of sI hydrate, it is likely that gas hydrate was inadvertently synthesized during the analysis. However, it is also possible that the low water content in the samples of approximately 26% produced too little natural gas hydrate for detection by the RGA method.

Conclusion

Unconsolidated well sorted quartz sandstone cores collected from Mt Elbert Stratigraphic Test Well #1 in early February (2007) were examined by HXRD. Sand dominated cores, collected from hydrate-rich zones were either preserved in LN₂ on site (HYD 8) or stored in a Parr vessel (with CH₄) at near reservoir conditions (HYD 21). As part of an effort to characterize physical attributes controlling the occurrence and stability of naturally occurring methane gas hydrate, *in situ* HXRD was used to monitor gas hydrate stability as a function of temperature. Physical properties such as moisture content, particle density, mineralogy, and gas hydrate saturation were determined in conjunction with HXRD.

Bulk dissociation experiments conducted on both core samples indicated natural gas hydrate was no longer present. Natural-occurring methane only appeared after the samples were held for extended periods out of the stability zone for gas hydrates, indicating the potential of biogenic methane production. Although the HXRD results indicate sI gas hydrate as in each core, it was likely a result of sample handling and pressurization and not originally present in the sediment.

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